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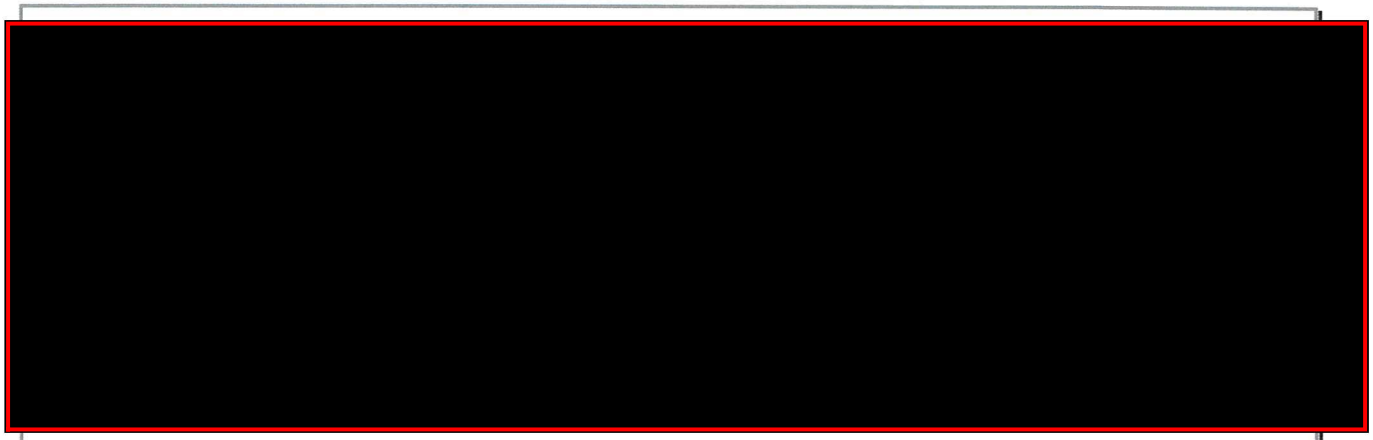
Title: Acid Digestion of Aqueous Samples for Metals Analysis by ICP



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1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the acid digestion of aqueous samples by EPA Method 200.7, SW-846 Method 3005A or SW-846 Method 3010A prior to the determination of the concentration of individual metallic elements by inductively coupled plasma atomic emission spectroscopy (ICP). These methods include digestions for total, total recoverable, dissolved, and potentially dissolved analytes (see definitions in Section 3).

1.2 This SOP is applicable to ground water, surface water, domestic and industrial wastewater, TCLP leachates, and other aqueous media. This SOP is not applicable to oils or other liquids that are not miscible with water.

NOTE: Samples that are found to be immiscible with water, e.g., contain oil or other immiscible organic solvents, are subcontracted to other labs that are capable of handling such samples. If during the preparation process it is discovered that the sample is immiscible with water or is biphasic, the analyst notifies the Technical Specialist and Project Manager, who can subcontract the samples to a laboratory with the capability to handle the sample.

1.3 The following table summarizes the applicability of the various digestion methods referenced in this SOP. All sample digestates are analyzed by ICP in accordance with SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

Method	Title	Summary	SOP Section
3005A/200.7_Prep	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP	Preparation of surface and ground water samples for total recoverable or dissolved metals for analysis by ICP.	10.5
3010A	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by ICP	Preparation of aqueous samples, EP and mobility procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.	10.8

1.4 Sample digestion requirements are established by the laboratory Project Manager before samples are received. TestAmerica LIMS (TALS) method codes are applied to samples at Login to indicate which digestion is to be used for each sample.

1.5 This procedure can be used for all of the elements listed in Table 1. Additional elements may be analyzed using the digestion methods in this SOP provided the method performance criteria specified in Section 12 and the Quality Control (QC) acceptance criteria specified in Section 9 of this SOP and the ICP determinative SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021 are met.

1.6 All samples require digestion prior to analysis, with the possible exception of "direct analysis" of dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples. This must be determined by the laboratory Project Manager before projects start, and is communicated to the analysts through Method Comments in TALS.

2.0 Summary of Method

2.1 Method 3005A/200.7_Prep, Total Recoverable, Dissolved Metals or Potentially Dissolved Metals

A representative portion of sample is heated with diluted nitric and hydrochloric acids until substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2 Method 3010A Total Metals

A representative portion of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary), and brought up to volume.

3.0 Definitions

3.1 Dissolved Analyte: The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter prior to acidification (sample is acidified after filtration).

3.2 Potentially Dissolved Metals: The concentration of elements in solution after acidifying the sample with nitric acid to pH < 2, holding at room temperature for 8 to 96 hours, and then filtering through a 0.45-µm membrane filter. This definition is based on the Colorado surface water regulations.

3.3 Total Recoverable Analyte: The concentration of analyte determined by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s).

3.4 Total Metals: The concentration of elements in an unfiltered sample subject to a more rigorous nitric acid / hydrochloric acid digestion than is used for total recoverable metals.

3.5 General Analytical Terms: Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, “Quality Assurance Program,” for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Potential sources of trace metals contamination include metallic or metal-containing labware (e.g., talc powdered gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work

areas, and atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not miscible with acids. If physical interferences are present, they should be documented in the final report case narrative.

4.3 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented in the final report case narrative.

4.4 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.5 Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample. Method 3005 or 3010 samples containing more than 1 mg/L silver are redigested at a reduced sample volume and reanalyzed to produce more accurate results. Method 200.7 requires samples to be redigested if the silver is greater than 0.1 mg/L.

4.6 Specific analytical interferences are discussed in the ICP determinative methods. See SOPs DV-MT-0012, DV-MT-0019, and DV-MT-0021.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 Samples that contain high concentrations of carbonates or organic material, or samples that are at elevated pH can react violently when acids are added.

5.3.3 Care must be taken when handling the digestion tubes. The tubes may become very hot during the digestion procedure. Allow the tubes to cool before attempting to touch the digested samples.

5.4 Primary Materials Used

5.4.1 The following is a list of the materials used in this method which have a serious or significant hazard rating.

5.4.2 A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time.

Material (1)	**Hazards**	**Exposure Limit(2)**	**Signs and Symptoms of Exposure**
Stock Standard Solutions	Oxidizer Corrosive Poison	5 mg/m^3 as HNO_3	Toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid (HNO_3)	Corrosive Oxidizer Poison	2 ppm (TWA) 4 ppm (STEL)	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid (HCl)	Corrosive Poison	5 ppm (Ceiling)	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Digestion blocks, with adjustable heating, capable of maintaining a sample temperature of 90 - 95 °C.

6.1.2 Thermometer that covers a temperature range of at least 80 - 110 °C, in increments of 1 °C.

6.1.3 Liquid-filled thermometers must have a tag indicating that the accuracy was checked by the QA group within the last 12 months.

6.1.4 Digital thermometers must have a tag showing that they were checked within the last three months.

6.1.5 See SOP DV-QA-0001 for details of the thermometer calibration procedure.

6.1.6 Centrifuge (when the desired method of removing particulates is centrifugation).

6.1.7 Calibrated mechanical pipettes with disposable pipette tips. Pipette calibration is checked in accordance with SOP DV-QA-0008.

6.2 Supplies

6.2.1 Disposable digestion tubes, with volume accuracy verified to ± 3% gravimetrically prior to use. See SOP DV-QA-0008.

6.2.2 Watch glasses, ribbed or equivalent, or disposable digestion tube covers.

6.2.3 Whatman GD/XP - PVDF membrane, 0.45-micron syringe filters (No. 6973-2504), for trace metal analysis, or equivalent. When used to filter any sample in a preparation batch or analytical batch, filters of the same type are also used to filter the method blank and the LCS in the batch. Acceptable results for the QC samples demonstrate that the filters neither add nor subtract analytes.

6.2.4 Syringes or equivalent filtration apparatus.

6.2.5 Re-pipettors or suitable reagent dispensers.

6.2.6 Class A volumetric graduated cylinders.

6.2.7 pH indicator strips.

6.2.8 Plastic digestate storage bottles.

7.0 Standards and Reagents

7.1 Standards must be NIST traceable, where available. Multi-element standards are verified against a second-source standard before they are put into use (the only exception is standards purchased directly from NIST), which is described in SOP DV-QA-0015.

7.2 Stock standards are purchased as custom multi-element mixes or as single-element solutions. Standards are logged into the TALS Reagent Module and are assigned unique identification numbers that can be used to access traceability information.

7.3 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles.

7.4 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.5 Standards containing silver must be protected from light using either a cardboard box or amber containers.

7.6 Shelf-Life

7.6.1 Stock standards, standards as received from the vendor, expire on the date assigned by the vendor. If no date is assigned by the vendor, then a one-year expiration will be assigned by the laboratory.

7.6.2 Intermediate concentration standards or working standards may be used for up to six months. The expiration date cannot be later than the date assigned to the stock standard.

7.6.3 Any suspect standards are re-verified, and replaced if re-verification fails.

7.7 Laboratory Control Sample (LCS) Spike Stock Standards

The LCS spike stock standards are custom-made standards purchased from Inorganic Ventures. The standards are designated ICP-SPK-3A (ICP-1) and ICP-SPK-2B (ICP-2) and contain the following elements at ready-to-use concentrations:

LCS Spike Stock Standards

Elements in LCS Spike	Concentration in ppm (µg/mL)
Ca, K, Mg, Na	5,000
P, Si	1,000

Elements in LCS Spike	Concentration in ppm (µg/mL)
Al, Ba, Bi, Se, Tl, U, Sn, S	200
Fe, Sr, Li, B, Mo, Ti, As, Th	100
Co, Mn, Ni, Pb, V, Zn, Sb, Zr	50
Cu	25
Cr	20
Cd	10
Ag, Be	5

7.8 TCLP Spike Stock Standard (TCLP Spike)

The TCLP spike stock standard is purchased from commercial sources. The stock is a custom-made standard purchased at ready-to-use concentrations and designated as TCLP Spike, as follows:

TCLP Spike Stock Standard

Elements in TCLP Spike	Concentration in ppm (µg/mL)
Ba	1,000
Cr, Pb	500
As	300
Cu, Zn	200
Ag, Cd, Se	100

7.9 TCLP Mercury Spike Solution

TCLP leachate matrix spike samples are spiked for both ICP elements and mercury at the time of sample preparation but before preservation. The mercury spike standard is prepared by the mercury analyst as the mercury daily spike solution (Hg Daily Spk) at a concentration of 100 µg/L (SOP DV-MT-0015).

7.10 Reagent Water

Reagent water must be produced by a Millipore de-ionized system or equivalent and must achieve the performance specifications for ASTM Type II water, i.e., conductivity < 1.0 µmhos/cm; resistivity > 1.0 megohms-cm; silica < 3.0 µg/L. In

addition, the reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs DV-MT-0012, DV-MT-0019, and DV-MT-0021.

7.11 Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.12 Hydrochloric acid (HCl), concentrated, trace metal grade or better.

8.0 Sample Collection, Preservation, Shipment and Storage

Preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	HDPE	500 mL	HNO_3, pH < 2	180 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD/DOE QSM 5.0 or 5.1 unless otherwise stated. Any deviation or exceptions from QSM 5.0 or 5.1 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.1 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. Ongoing proficiency must be demonstrated by each analyst on an annual basis. See Section 12 for more details on initial demonstrations of capability, analyst training and qualification.

9.2 Preparation Batch

A preparation batch is a group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, a matrix spike (MS), and a matrix spike duplicate (MSD). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for the MS/MSD pair, then the batch may contain multiple MS/MSD pairs to accommodate client requests. Clients may also request a duplicate LCS (LCSD). In cases where the client has not provided sufficient sample to prepare an MS and MSD, an LCS and LCSD will be prepared instead.

9.3 Sample Count

Laboratory-generated QC samples (method blanks, LCSs) are not included in the sample count for determining the size of a preparation batch. The MS and MSD are not included in the sample count unless specifically requested by the client. The prep batch consist of the laboratory generated QC and no more than twenty field samples.

9.4 Method Blank (MB)

9.4.1 The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. When samples are filtered in the laboratory for determination of dissolved metals, then the blank is filtered using a filter of the same type that was used for the samples.

9.4.2 TCLP method blanks are prepared by taking 10 mL of TCLP leachate fluid (see SOP DV-IP-0012) through the appropriate procedure as described in Section 10. TCLP method blanks are referred to as LB (extraction fluid 1) and LB2 (extraction fluid 2) in TALS and on the final reports.

9.4.3 One method blank must be processed with each preparation batch. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false-positive data. Method blank results are evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

9.4.4 Acceptance Criteria

The method blank should not contain any analyte of interest at or above ½ the reporting limit (RL) or at or above 10% of the measured concentration of that analyte in associated samples, whichever is higher. In other words, the sample result must be a minimum of 10 times higher than the blank contamination level. Method blank results that are greater than ½ the RL may also be reported if the associated sample results fall below the RL and the client accepts the data.

9.4.5 Corrective Action

If the method blank does not meet the acceptance criteria, the blank and all associated samples in the batch must be re-digested and reanalyzed.

9.5 Laboratory Control Sample (LCS)

9.5.1 One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. When samples are filtered in the laboratory for determination of dissolved metals, then the LCS is filtered using a filter of the same type that was used for the samples.

9.5.2 An LCS for a batch of aqueous samples is prepared by adding 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to 50 mL of reagent water. This produces the final concentrations shown in Table 1.

9.5.3 An LCS for a TCLP batch is prepared by adding 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), plus 0.5 mL of the TCLP Spike stock standard (Section 7.8) to 50 mL of the TCLP leachate solution (see SOP DV-IP-0012). This produces the final concentrations shown in Table 2.

9.5.4 The LCS is used to monitor the accuracy of the analytical process. LCS results are evaluated by the ICP analyst as described in SOP DV-MT-0012. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.5.5 Acceptance Criteria

LCS recovery control limits are set at ± 3 standard deviations about the historical mean. These limits must not be wider than 85 - 115 % recovery

for Method 200.7 or 80 - 120 % for Method 6010. The control limits are maintained in the LIMS system.

9.5.6 Corrective Action

If the LCS percent recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples. This latter case must be documented in an NCM and explained in the case narrative.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Normally, one MS/MSD pair is digested with each preparation batch. Samples identified as field blanks, equipment blanks, or rinse blanks are not appropriate for use as the batch MS/MSD.

9.6.2 Some programs (e.g., South Carolina and North Carolina) require that MS/MSD pairs are run at a 10% frequency. Also, some clients may require unspiked duplicate samples in place of or in addition to an MS/MSD pair. Check special project instructions attached as Method Comments in TALS and any project QASs before starting the batch.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD precision is preferred as not all samples will contain measurable concentrations of target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, the LCS and LCSD are used to measure precision.

9.6.3 If insufficient sample is available to process an MS/MSD pair, then a duplicate LCS must be processed and an NCM generated. The LCS pair is then evaluated according to the MS/MSD criteria. DoD requires the MS/MSD to be assigned by the client. When there is no assigned MS/MSD or there is not enough sample volume provided an LCSD must be prepared.

9.6.4 The purpose of analyzing matrix spike samples is to assess the effect of the sample matrix on the accuracy and precision of the analysis. MS/MSD results are evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021. If the MS/MSD results fail to meet control limits while the LCS results are in control, then something about the sample matrix is interfering with the analysis.

9.6.5 Matrix spikes for aqueous sample batches are prepared by adding 0.5

mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to a digestion tube containing 50 mL of the selected sample. The final spike concentrations are shown in Table 1.

9.6.6 Matrix spikes for TCLP batches are prepared by adding 0.5 mL of the TCLP Spike stock standard (Section 7.8) plus 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to 50 mL of the parent TCLP aliquot. A second aliquot is spiked for mercury analysis at by adding 1.5 mL of the 100 mg/L Hg standard (Hg Daily Spk) to 30ml of parent sample. The matrix spike samples are then preserved with HNO_3 to pH < 2. The final spike concentrations are shown in Table 2.

NOTE: The MS and MSD must be spiked prior to preservation of the leachate.

9.6.7 Acceptance Criteria

The recovery for each analyte must fall within established limits. The relative percent difference (RPD) between the MS and MSD must be less than or equal to the established RPD limit. If any analyte recovery or relative percent difference (RPD) between the MS and MSD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS.

9.6.8 Corrective Action

If MS/MSD results fail to meet control limits, but the LCS results are within limits, then samples do not require re-preparation and reanalysis unless the results indicate that a spiking error may have occurred. If the recovery of the LCS also failed acceptance criteria, then corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. One possible exception is an LCS recovery for a given element above the upper control limit with no detection for the same element in the samples. This latter case must be documented in an NCM and explained in the case narrative.

9.7 Continuing Calibration Verification Standard (CCV)

Continuing calibration verification standards (CCVs) are not digested but are instead created and evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

9.8 Second-Source Initial Calibration Verification (ICV) Standard

Initial calibration verification standards (ICVs) are not digested but are instead created and evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 All data shall be recorded directly on the described forms, logbooks, electronic forms, or directly in TALS at the time of data generation. It is not acceptable to record data on loose papers, scraps of paper, gloves, sample vials, or "Post-It" notes. Data may be recorded on paper bench sheets if the sheets are subsequently scanned and saved in a designated folder on the company server.

10.4 All equipment IDs for any support equipment (pipettes, thermometers, etc.) must be recorded in the batch record.

10.5 Sample Preparation

10.5.1 Samples are typically logged in as either water or solid. Waste such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating sample preparation, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous, but it appears to be a waste (biphasic, oil, sludge-like, organic liquid, lots of sediment, etc.), contact the project manager and the laboratory Technical Specialist for further instructions. It may be necessary to subcontract these samples to a laboratory with the capability to digest organic matrices.

NOTE: TestAmerica Denver has not implemented digestion methods for water-immiscible organic matrices, e.g., oils. Samples that are known to be incompatible with TestAmerica Denver digestion techniques are typically subcontracted to other laboratories.

10.5.2 All samples are to be electronically checked out of sample control using the TALS Internal Chain of Custody (ICOC) module.

10.5.3 Proper sample identification is extremely important in any preparation procedure. Labeling of beakers, digestion tubes, and bottles must be done in a manner to ensure connection with the proper sample.

10.5.4 If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab, data review and reporting.

10.5.5 Guidelines are provided in Appendix 1 on procedures to minimize contamination of samples and standards.

10.6 Aqueous Sample Preparation Setup

The following setup procedure must be followed for all aqueous samples prior to performing the specific digestion procedure. The sample preparation procedures for Methods 3005A and 3010A detailed in the following sections are also summarized in work instruction WI-DV-016.

10.6.1 Verify sample pH

10.6.1.1 Measure the sample pH with pH paper using a separate aliquot of sample. This can be done using disposable plastic droppers or pouring the sample on to the pH paper. Do not put the pH paper directly into the bottle. Record the pH on a copy of the internal chain of custody (ICOC). When all of the samples have been tested, initial and date the copy of the ICOC, scan it, and save it to the Metals folder on the G: drive.

10.6.1.2 All water sample pH's must be verified and documented in the batch record before digestion.

10.6.1.3 If the pH>2 for a sample requiring acidic preservation, record the job in the Sample Filtration and Preservation Logbook.

10.6.1.4 If laboratory preservation is required, add 1-2 mL of conc. HNO_3 to the sample. Replace the lid and mix the sample. If the pH is still >2 add another addition of HNO_3. Do not add more than 5 mL. If the pH is still >2 create an NCM saying the sample will not preserve.

10.6.1.5 Allow the sample to sit for 24 hours following acidification.

10.6.1.6 Recheck the pH of the sample. If the pH>2, repeat Section 10.5.1.4 until the pH holds at <2 or 5 mL of HNO_3 has been added. If the pH is still >2 after the addition of 5 mL of HNO_3 create an NCM saying the sample will not preserve.

10.6.1.7 Samples cannot be digested for 24 hours after preservation. Note the date/time of this pH recheck in the Metals Prep Log in the LIMS.

10.6.1.8 Leachates or portions of leachates for metallic analyte deteminations must be acidified with nitric acid to a pH <2 unless precipitation occurs. Test a small portion of sample to see if precipitation occurs. If a precipitate forms do not acidify the leachate and analyze as soon a possible. Leachates may be digested as soon as they are acidified.

10.6.2 Select the unfiltered fraction for a total or total recoverable analysis or the

filtered fraction for a dissolved analysis. If requested by the client, select the filtered fraction for a total dissolved analysis. For TCLP and SPLP, select the proper sample leachates.

10.6.2.1.1 Samples requiring dissolved metals determination are either filtered and preserved in the field or are filtered and preserved by the laboratory as soon as possible after receiving the samples. When filtered in the laboratory, the filtration and preservation are recorded in the Laboratory Sample Filtration and Preservation Logbook, including the preservative type and lot number.

10.6.2.1.2 Samples and batch QC requiring filtration are to be put into a filtration batch. A filtration batch is to have no more than 20 samples.

10.6.2.1.3 Filter acceptability is demonstrated by using filters of the same type to filter samples and batch QC samples when preparation batches include samples that were filtered in the laboratory. The results of the analysis of the batch QC samples are used to demonstrate that the filtration process neither adds nor subtracts target analytes from samples. The performance of the filtration process is recorded in TALS.

10.6.3 Mix the sample by shaking the container.

10.6.4 Measure and transfer 50 mL of the sample into a digestion tube (record the lot number of the digestion tubes used in the LIMS). When using calibrated digestion tubes, pour the sample into the tube to the 50 mL mark. For TCLP sample batches pour 10 mL of samples and bring to 50 mL with reagent water. Unless specifically required for a project, all samples are measured by volume and not by weight. Record the volume and units on the preparation bench sheet in TALS. If the digestion cup is filled beyond the required mark, the excess sample must not be poured back into the original container, but must be disposed of as waste.

10.6.5 Mix the sample by shaking the container and then measure two extra aliquots of the sample that is selected for the MS/MSD analysis. Spike each aliquot as described in Section 9.6. Refer to Section 9.6.6 for specific instructions for spiking the selected TCLP sample. Record the standards and pipette identifications in TALS.

10.6.6 Measure and transfer 50 mL of reagent water into a digestion tube for the method blank. If a determination of dissolved metals is requested (LIMS 3005A), use filtered reagent water for the method blank. For TCLP sample batches, measure 10 mL of the TCLP leachate solution and bring to 50 mL with reagent water for the blank. See Section 9.4 for a detailed description of the method blank.

10.6.7 Measure and transfer 50 mL of reagent water into a digestion tube for the

LCS and add the spiking solutions as described in Section 9.6.2. For TCLP sample batches, use 10 mL of TCLP leachate fluid and bring to a final volume of 50ml with reagent water for preparing the LCS (Section 9.5.3). Record the standards and pipette identifications in TALS. If determination of dissolved metals is requested and one or more samples were filtered in the laboratory, then filter the LCS using a filter of the same type that was used to filter the sample(s).

10.6.8 If the analysis is for total recoverable, dissolved metals, or potentially dissolved metals, continue on with Section 10.5. If the analysis is for total metals, skip Section 10.6 and go to Section 10.7.

10.7 Total Recoverable, Dissolved, or Potentially Dissolved Digestion for Waters by 3005A and 200.7_Prep.

10.7.1 Add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl to the sample in the digestion tube.

10.7.2 Heat at 90-95 °C until the volume is reduced to between 15 and 20 mL. Record the start and stop times, digestion block temperature (observed and corrected) and the thermometer ID in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.7.3 Allow the digestion tube to cool in a fume hood.

10.7.4 Wash down the digestion tube walls with reagent water.

10.7.5 Add 1.5 mL of concentrated HNO_3 to the digestate.

10.7.6 Revolume to 50 mL with reagent water. Cap and shake to mix.

10.7.7 If insoluble materials are present, the sample will be filtered at the instrument by the analyst.

NOTES: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Instead of filtering, the samples may be diluted and mixed and then centrifuged or allowed to settle overnight to remove insoluble material from the supernatant solution.

10.7.8 The sample is now ready for analysis.

10.8 Total Metals Digestion for Waters or TCLP Leachates by 3010A

10.8.1 Add 1.5 mL of concentrated HNO_3 to the sample in the digestion tube.

10.8.2 Heat at 90-95 °C until volume is reduced to 10 ± 5 mL. Record the start and stop times, digestion block temperature (observed and corrected) and the thermometer ID in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.8.3 Allow the digestion tube to cool in a fume hood.

10.8.4 Add another 1.5 mL portion of concentrated HNO_3 and cover the sample with a watchglass.

10.8.5 Continue refluxing until the digestion is complete.

NOTE: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient. Additional aliquots of nitric acid may be added if necessary.

10.8.6 Evaporate to a low volume of 5 to 10 mL. If the sample does go to dryness, the digestion must be started over using a fresh portion of sample.

10.8.7 Allow the digestion tube to cool in a fume hood.

10.8.8 Add 2.5 mL of concentrated HCl.

10.8.9 Cover and reflux for an additional 15 minutes to dissolve any precipitate or residue.

10.8.10 Wash down the digestion tube walls and watch glass (or digestion tube cover) with reagent water.

10.8.11 Adjust to 50 mL final volume with reagent water. This must be done volumetrically, and not using a balance.

10.8.12 If insoluble materials are present, the sample will be filtered at the instrument by the analyst.

NOTES: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Instead of filtering, the samples may be diluted and mixed and then centrifuged or allowed to settle overnight to remove insoluble material from the supernatant solution.

10.8.13 The sample is now ready for analysis.

10.9 Calibration

10.9.1 The digestion block temperature must be maintained between 90 and 95 °C. The temperature must be monitored continuously while in use and must be recorded in TALS. The temperature must be monitored by measuring the temperature of reagent water contained in a capped digestion tube that is placed in each digestion block. The thermometer used and the start and end times for all temperature cycles are recorded in TALS.

10.9.2 The thermometer is calibrated in accordance with SOP DV-QA-0001, Thermometer Calibration Procedures.

11.0 Calculations / Data Reduction

11.1 This SOP does not produce any analytical data. See the determinative method SOPs DV-MT-0012, DV-MT-0019 or DV-MT-0021 for data analysis and applicable calculations.

11.2 Documentation

11.2.1 All of the preparation information is recorded and stored in TALS.

11.2.2 The preparation information includes:

11.2.2.1 Batch number, job and sample numbers, preparation date, and analyst name;

11.2.2.2 Matrix and prep type;

11.2.2.3 Initial sample pH, Initial sample volume and final volume;

11.2.2.4 Reagent manufacturer and lot number for each reagent used;

11.2.2.5 Digestion tube lot information;

11.2.2.6 Standard identification number for each standard used;

11.2.2.7 Start and stop times for digestions;

11.2.2.8 Observed and corrected temperature readings during digestion;

11.2.2.9 Identification numbers of calibrated measuring equipment used (thermometers, balances, pipettes, etc.).

11.3 Reporting

11.3.1 Reporting units are mg/L for water samples.

11.3.2 If dilutions were required due to insufficient sample, interferences, or other problems, the reporting limit is multiplied by the dilution factor, and the data may require flagging.

11.3.3 All associated data are entered or uploaded into the LIMS as required.

NOTE: Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

11.4 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for more detail on the review process.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD and DOE projects, an MDL verification is performed quarterly.

12.1.2 The current MDL value is maintained in TALS.

12.2 Limit of Quantitation Verification (LOQV)

The verification of the limit of quantitation (LOQ or LLOQ) is performed quarterly for work performed according to the DOD/DOE QSM 5.0 or 5.1. A blank matrix is spiked at 1-2 the laboratory RL and carried through the entire preparation and analytical procedures. Recoveries are assessed based on historical limits.

12.3 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.3.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

12.3.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.3.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.3.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.3.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.4 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

13.1 This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards: Contact Waste Coordinator

14.2.2 Acidic waste from sample digests: Waste Stream J.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.1.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.2 Method 3010A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.2 Method 200.7, Determination of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, 1994.

16.0 Method Modifications

16.1 Modifications Specific to MCAWW Methods (200.7_Prep)

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 10.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness versus an exact volume).

16.2 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit. Common laboratory contaminants are allowed up to the reporting limit in the blank following consultation with the client.

16.3 The referenced methods use 100 mL of sample for digestion. This SOP uses a 50 mL aliquot, with a proportional reduction in digestion reagents. This change is made to allow better control of temperature and potential sample contamination with the use of the digestion block. It is also considered one of the laboratory's hazardous waste reduction initiatives.

16.4 The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document states "flexibility to alter digestion volumes is addressed and 'allowed' by the table (3-1)

and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.0 Attachments

Table 1. Matrix Spike and Aqueous Laboratory Control Sample Levels

Table 2. TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

Appendix 1. Contamination Control Guidelines

18.0 Revision History

- Revision 10 dated 30 June 2017
  - Annual technical review
  - Updated Section 9.1.2 to include QSM 5.1
  - Added current Section 10.4 referencing support equipment IDs and renumbered remaining sections
  - Added Sections 11.3 and 11.4
  - Updated Section 12.1.1 MDLV language for consistency with other SOPs
  - Added current Section 12.2 regarding LOQVs and renumbered remaining sections
  - Updated the language in Sections 12.3 and 12.4 for consistency with other SOPs

- Revision 9 dated 30 June 2016
  - Annual technical review
  - Added "document in the batch record" regarding sample pH to Section 10.5.1.2.
  - Updated Section 9.5.2 to say 10ml of TCLP fluid is added to the method blank.
  - Updated Section 10.5.1.5 to wait 24 hours after acidification before checking pH
  - Converted the note in Section 10.5.2 into subsections 10.5.2.1.1 - 10.5.2.1.3
  - Added definition of filtration batch to section 10.5.2.1.2
  - Updated Section 16.2 to say we control common laboratory contaminates to the reporting limit.
-
- Revision 8 dated 30 June 2015
  - Updated Section 10.5.1.1 to include statement about not putting the pH paper into the bottle
  - Added language to Section 4.5 for clarification
  - Added new Section 10.3 reminding analysts to enter data directly at time of acquisition

- Revision 7 dated 31 October 2014
  - Annual technical review
  - Removed reference to SOP DV-IP-0017 for oils in section 1.2
  - Added maximum silver concentration to section 4.5 for method 200.7
  - Updated standard ID's for sections 7.7 and 7.8 and added Sulfur to the spike list
  - Corrected intermediate standard expirations from three months to six months
  - Removed duplicate analyte spike levels in ICP spike standards
  - Changed references from LIMS to TALS
  - Corrected concentration of Hg Daily spike standard
  - Removed Figures 1 and 2
  - Corrected various grammar and language errors
  - Corrected analyte spike levels in Table 1

- Revision 6 dated 08 October 2013
  - Updated sections 10.4.1.3, 10.4.1.4 and 10.4.1.6 about preservation procedure and removed the comment about recording the amount of acid added in the preservation logbook

- Revision 5, dated 15 July 2013
  - Annual review
  - Changed section 10.5.5, 7.3, 9.4, 9.5.2, 9.5.4, 10.3.1, 10.3.2, 10.4, 10.4.4, 10.5.2, 10.6.2, 11.2.2, 12.1.1 and 12.3 to reflect current practices
  - Corrected formatting and grammatical errors
  - Clarified sample matrices for this method in section 1.2
  - Corrected references in table associated with section 1.3
  - Added ICP determinative SOPs to sections 1.5, 4.6, 7.10, 9.5.3, 9.7.4
  - Added 200.7_Prep whenever 3005A was referenced
  - Edited section 3.5 to reflect current reference
  - Removed note associated with section 5.4.1
  - Added SOP reference to section 6.2.1
  - Removed references to Denver Standards Log and replaces those references with TALS reagent module
  - Correct standard names in section 7.7
  - Removed references to Supplemental Metals Prep Sheet
  - Updated sections 10.4.4, 10.4.6 and 10.4.7 for 10 mL TCLP sample aliquot
  - Added reference to 200.7 in Section 15

- Revision 4.7, dated 18 July 2012
  - Annual review
  - Updated Section 9.1, 10.1 and 10.2 to reflect current practice
  - Updated Section 9.7.6 on spiking TCLP aliquots
  - Added section 10.4.1.9 for TCLP preservation
  - Removed Appendix 2. Added reference to work instruction in Section 10.4
  - Updated Figures 1 and 2 to reflect current practice.
  - Formatting and editorial changes throughout

- Revision 4.6, dated 24 August 2011
  - Added recommendation to use disposable bulbs for pH checking in section 10.8.1.
  - Added requirement to store samples with a Rush form after preserving in section 10.8.1.2.

- Revision 4.5, dated 31 January 2011
  - Change note in section 10.8.1.8 to be 24 hours before preparation.

Earlier revision histories have been archived and are available upon request.

Table 1.

Matrix Spike and Aqueous Laboratory Control Sample Levels

Element	LCS Concentration (ug/L)	Matrix Spike Concentration (ug/L)
Aluminum	2,000	2,000
Antimony	500	500
Arsenic	1,000	1,000
Barium	2,000	2,000
Beryllium	50	50
Bismuth	2,000	2,000
Boron	1,000	1,000
Cadmium	100	100
Calcium	50,000	50,000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	1,000
Lead	500	500
Lithium	1,000	1,000
Magnesium	50,000	50,000
Manganese	500	500
Molybdenum	1,000	1,000
Nickel	500	500
Phosphorous	10,000	10,000
Potassium	50,000	50,000
Selenium	2,000	2,000
Silicon	10,000	10,000
Si (as SiO2)	21,400	21,400
Silver	50	50
Sodium	50,000	50,000
Strontium	1,000	1,000
Thallium	2,000	2,000
Tin	2,000	2,000
Titanium	1,000	1,000
Uranium	2,000	2,000
Vanadium	500	500
Zinc	500	500
Zirconium	500	500

Table 2.

TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

Element	RL (mg/L)	Regulatory Limit (mg/L)	Spike Level (mg/L)
Arsenic	0.1	5,000	5.0
Barium	1.0	100,000	12.0
Cadmium	0.05	1,000	1.05
Chromium	1.0	5,000	5.2
Lead	0.03	5,000	5.5
Selenium	0.05	1,000	3.0
Silver	0.1	5,000	1.05

Appendix 1.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Electronic Copy Only

Title: Acid digestion of Aqueous Samples for Analysis by ICP- MS [SW-846 3005A, 3020A, and EPA Method 200.8.]

Approvals (Signature/Date):

[redacted]

Facility Distribution No. _____ **Distributed To:_____**

1.0 Scope and Application

1.1 This procedure describes the preparation of aqueous samples for the analysis of metals by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) using EPA Method 200.8, and SW-846 Methods 3005A and 3020A.

1.2 Aqueous samples also include TCLP & SPLP Leachates, aqueous equipment rinse blanks for soil sampling. In some cases, where the associated soil samples require the SW-846 Method 3050B, Section 7.5, optional treatment to improve solubility and recovery of Sb, Ag, and Sn, the client may require that the aqueous equipment blank receive the same treatment. Refer to section 10.14 for this prep.

1.3 The applicability of each of these preparation protocols to specific analytes is detailed in the TestAmerica LIMS System (TALS). Additional elements may be analyzed following digestion by these protocols, provided that the method performance criteria specified in Section 12.0 of this SOP are met.

1.4 This SOP provides procedures applicable to the preparation of dissolved, total recoverable, potentially dissolved, and total metallic elements in ground water, aqueous samples, aqueous sludges, aqueous wastes, aqueous air sampling media, and leachates/extracts. This SOP is not applicable to samples that contain or consist of oil or other immiscible organic solvents.

NOTE: Samples that are known to be immiscible with water, e.g., contain or consist of oil or other immiscible organic solvents should be logged with a waste matrix and subbed out to a different TestAmerica laboratory for digestion and analysis.

1.5 SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP-MS. Although digestion is not specifically required by the method (SW-846 3005A section 2.2) for dissolved samples, the standard operating procedure at TestAmerica Denver is for all matrices to be digested prior to analysis.

1.6 EPA Method 200.8 Section 11.2 is used to prepare surface water, drinking water, and domestic and industrial waste samples for total recoverable and dissolved metals.

1.7 SW-846 Method 3020A is used to prepare aqueous samples, TCLP leachates, SPLP leachates and aqueous wastes that contain suspended solids for total metals analysis by ICP-MS.

1.8 The following table lists the sample preparation methods that are covered in this SOP and the specific section of this SOP for each preparation method. Prepared samples are analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

PREPARATION METHOD	SOP SECTION	DETERMINATIVE METHOD	ANALYTICAL SOPS #
Method – 3020A Total	10.11	ICP-MS	DV-MT-0018 DV-MT-0022
Method – 3005A Total Rec./Dissolved	10.12	ICP-MS	DV-MT-0018 DV-MT-0022
Method 200.8 – Total Rec.	10.13	ICP-MS	DV-MT-0002
Method 200.8 – Dissolved	10.13	ICP-MS	DV-MT-0002
Method - 3050B Special Sb Prep	10.14	ICP-MS	DV-MT-0018 DV-MT-0022

2.0 Summary of Method

2.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals.

This preparation method is used for total recoverable and dissolved metals analysis by ICP-MS method 6020 and 6020A. A representative aliquot of sample is heated with nitric acid and substantially reduced in volume. The digestate is diluted to volume and then filtered (if necessary).

2.2 Method 3020A, Acid Digestion of Aqueous Samples and TCLP/SPLP Leachates for Total Metals.

This preparation method is used for total metals analysis by ICP-MS method 6020 and 6020A. A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. The digestate is diluted to volume and then filtered (if necessary).

2.3 Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry.

This preparation method is used for metals analysis by ICP-MS method 200.8. A representative aliquot of sample is refluxed with nitric and hydrochloric acids. The digestate is diluted to volume and then filtered (if necessary).

3.0 Definitions

Additional definitions of terms used in this SOP may be found in the glossary of the QAM.

- Dissolved Metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-μm membrane (Method 3005A). (The sample is acidified after filtration).

- Total Metals: The concentration of metals determined in an unfiltered sample following digestion (Method 3020A).

- Total Recoverable Metals: The concentration of metals determined in an unfiltered sample following treatment with hot, dilute mineral acid (Method 200.8 and Method 3005A).

- Potentially Dissolved Metals: An acidified sample is filtered between 8- 96 hours following acidification and the filtrate is digested using Method 3005A.

- Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include the following: metallic or metal-containing labware (e.g., latex gloves coated with talc, which contains high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix A for additional contamination control guidelines.

4.3 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not soluble in acids. If physical interferences are present, they should be documented.

4.4 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.5 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared.

4.6 Specific analytical interferences are discussed in the ICP-MS determinative method SOPs, e.g., DV-MT-0002, DV-MT-0018, and DV-MT-0022.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, and this document.

5.1 Specific Safety Concerns

5.1.1 Samples that contain high concentrations of carbonates or organic material, or samples that are at elevated pH can react violently when acids

are added.

5.1.2 The digestion solution must be cooled sufficiently before adding hydrogen peroxide (H_2O_2) to avoid a reaction and possible violent effervescence, or boiling over of the digestion solution.

5.1.3 Care must be taken when handling the digestion tubes. The tubes may become very hot during the digestion procedure. Allow the tubes to cool before attempting to touch the sample digestate.

5.1.4 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [1]	Hazards	Exposure Limit [2]	Signs and Symptoms of Exposure
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm (TWA)	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm (TWA) 4 ppm (STEL)	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage

Material [1]	Hazards	Exposure Limit [2]	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5 ppm (Ceiling)	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Digestion block, with adjustable heating, capable of maintaining a sample temperature of 85 - 95 °C.

6.1.2 Thermometer that covers a temperature range of at least 80 - 110 °C.

6.1.3 Centrifugation equipment (if desired method of removing particulate material is centrifugation).

6.2 Supplies

6.2.1 Disposable digestion tubes, with volume accuracy verified to ± 3% gravimetrically prior to use. See SOP DV-QA-0008.

6.2.2 Watch glasses, ribbed or equivalent, or disposable digestion tube covers.

6.2.3 Whatman GD/XP - PVDF membrane, 0.45-micron syringe filters, No. 6973-2504, for trace metal analysis, or equivalent. When used to filter any sample in a preparation batch or analytical batch, filters of the same type are also used to filter the method blank and the LCS in the batch. Acceptable results for the QC samples demonstrate that the filters neither add nor subtract analytes.

6.2.4 Syringes or equivalent filtration apparatus.

6.2.5 Repipettors or suitable reagent dispensers.

6.2.6 Calibrated automatic pipettes with pipette tips or Class A glass volumetric pipettes.

6.2.7 Class A volumetric flasks.

6.2.8 pH indicator strips (pH range 0 - 6).

6.2.9 Plastic digestate storage bottles.

7.0 Reagents and Standards

7.1 Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative method SOPs, e.g., DV-MT-0002, DV-MT-0018, and DV-MT-0022.

7.2 Laboratory control sample (LCS), and matrix spike and matrix spike duplicate (MS/MSD) spike solutions are purchased as custom TestAmerica Denver solutions. Standards are logged into the Reagents module of TALS and are assigned unique identification numbers that can be used to access traceability information. The TALS identification numbers are recorded on the metals prep bench sheet.

7.2.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. These plastic bottles may be stored in a glass jar.

7.2.2 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.2.3 See TALS for the list of spiking levels. A volume of 0.1 mL of each working spike solution is added to the 50-mL final sample volume.

7.3 Nitric Acid (HNO_3), concentrated, trace-metal grade or better.

NOTE: When preparing diluted acids, always add acid to water. If the water is added to the acid, the sudden increase in temperature may cause splashing.

7.4 Nitric Acid, 1:1

Dilute concentrated HNO_3 with an equal volume of reagent water.

7.5 30% Hydrogen Peroxide (H_2O_2), ultra pure grade.

7.6 Hydrochloric Acid (HCl), concentrated, trace metal grade or better.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE Or Glass	500 mL	HNO_3, pH < 2	180 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS login, sample or method comments and/or program QAS to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified appropriately. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Table 2 provides a summary of quality control requirements, including type, frequency, acceptance criteria, and corrective action. Detailed information regarding acceptance criteria and corrective action are found in each determinative method SOP.

9.3 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. Ongoing proficiency must be demonstrated by each analyst on an annual basis. See

Section 12.1 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.4 Preparation Batch

A preparation batch is a group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, a matrix spike (MS), and a matrix spike duplicate (MSD). For samples logged in under Method 200.8, there must be two MS/MSD pairs for every batch containing more than ten samples. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for the MS/MSD pair, then the batch may contain multiple MS/MSD pairs to accommodate client requests. Clients may also request a duplicate LCS (LCSD). In cases where the client has not provided sufficient sample to prepare an MS and MSD, an LCS and LCSD will be prepared instead.

9.5 Sample Count

Laboratory-generated QC samples (method blanks, LCSs) are not included in the sample count for determining the size of a preparation batch. The MS and MSD are usually not included in the sample count.

9.6 Method Blank (MB)

The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. When samples are filtered in the laboratory for determination of dissolved metals, then the blank is filtered using a filter of the same type that was used for the samples. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false-positive data.

9.7 Laboratory Control Sample (LCS)

One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. When samples are filtered in the laboratory for determination of dissolved metals, then the LCS is filtered using a filter of the same type that was used for the samples. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs)

may require the use of sample duplicates in place of or in addition to MS/MSDs. At least one MS/MSD pair must be processed for each preparation batch. Some client programs require a 10 % MS/MSD analysis frequency. If insufficient sample is available to process an MS/MSD pair, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks, equipment blanks, or rinse blanks cannot be used for MS/MSD analysis.

9.9 Quality Assurance Summaries

Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QASs) are developed to address these requirements.

10.0 Procedure

Sample Preparation

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervisors to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3 All samples are to be checked out of Sample Control with the Internal Chain of Custody in TALS properly completed.

10.4 Proper sample identification is extremely important in any preparation procedure. Labeling of beakers, digestion tubes, and bottles must be done in a manner to ensure connection with the proper sample.

10.5 Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating sample preparation, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous, but it appears to be more like a waste (biphasic, oil, sludge-like, organic liquid, lots of sediment, etc.), then contact the project manager and the laboratory group leader for further instructions.

10.6 If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab, data review, and reporting groups.

10.7 Guidelines are provided in Appendix A on procedures to minimize contamination of samples and standards.

10.8 All data shall be recorded directly on the described forms, logbooks, electronic forms, or directly in TALS at the time of data generation. It is not acceptable to record data on loose papers, scraps of paper, gloves, sample vials, or "Post-It" notes. Data may be recorded on paper bench sheets if the sheets are subsequently scanned and saved in a designated folder on the company server.

10.9 Aqueous Sample Preparation Setup

The following setup procedure must be followed for all aqueous samples prior to performing the specific digestion procedure:

10.9.1 Sample pH is verified during sample receipt. When a sample is received with improper/insufficient preservation, the sample is delivered with notification of the deficiency.

10.9.1.1 Measure the sample pH with pH paper using a separate aliquot of sample. Do not put the pH paper directly into to bottle. Record the pH on a copy of the internal chain of custody (ICOC). When all of the samples have been tested, initial and date the copy of the ICOC, scan it, and save it to the Metals folder on the G: drive.

10.9.1.2 If the pH>2 for a sample requiring acidic preservation, add 1-2 mL of conc. HNO_3 to the sample. Replace the lid and mix.

10.9.1.3 Recheck the pH of the sample. If the pH<2, record the sample in the Metals preservation logbook. If the pH>2, repeat 10.9.1.2 until pH<2 or 5mls has been added. If the sample still has a pH greater than 2 do not add any additional acid and create an NCM. Add the sample to the Metals preservation logbook

10.9.1.4 Allow the sample to sit for 24 hours following acidification.

10.9.1.5 After 8-16 hours, recheck the pH of the sample. If the pH<2, proceed with the appropriate digestion procedure. Note the date/time of this pH recheck in the Metals preservation logbook.

10.9.1.6 If after 8-16 hours the pH>2, repeat steps 10.9.1.2 through 10.9.1.5 until the pH remains <2 following the 8-16 hour period or 5mls of HNO_3 has been added.

Note: Acid must be added at least 24 hours before analysis.

10.9.2 Select the unfiltered fraction for a total or total recoverable analysis or the

filtered fraction for a dissolved analysis. For SPLP select the proper sample leachates.

NOTE: Samples requiring dissolved metals determination are either filtered and preserved in the field or are filtered and preserved by the laboratory as soon as possible after receiving the samples. When filtered in the laboratory, the filtration and preservation are recorded in the Laboratory Sample Filtration and Preservation Logbook, including the preservative type and lot number. Filter acceptability is demonstrated by using filters of the same type to filter samples and batch QC samples when preparation batches include samples that were filtered in the laboratory. The results of the analysis of the batch QC samples are used to demonstrate that the filtration process neither adds nor subtracts target analytes from samples.

10.9.3 Mix the sample by shaking the container.

10.9.4 Measure and transfer 50 mL of the sample into a digestion tube. When using calibrated digestion tubes, pour the sample into the tube to the 50-mL mark. Record the lot number of the digestion tubes in TALS.

10.9.5 Measure two extra aliquots of the sample that is selected for the MS/MSD analysis. Spike each aliquot with 0.1 mL of each spiking solution (see TALS). Record the standards and pipette identifications in TALS.

10.9.6 Measure and transfer 50 mL of reagent water into a digestion tube for the method blank. If a determination of dissolved metals is requested, use filtered reagent water for the method blank.

10.9.7 Measure and transfer 50 mL of reagent water into a digestion tube for the LCS and add 0.1 mL of spiking solution (see Table 2). Record the standards and pipette identifications in TALS. If determination of dissolved metals is requested (preparation method 3005A), and one or more samples were filtered in the laboratory, then filter the LCS and Method Blank using a filter of the same type that was used to filter the sample(s).

10.10 Proceed to the appropriate Section of this SOP for the desired preparation method as follows:

Preparation Method*	SOP Section	Analytical Method
3020A Total Metals	10.11	Method 6020
3005A Total Recoverable	10.12	Method 6020
3005A Dissolved Metals	10.12	Method 6020
200.8 Total Recoverable Metals	10.13	Method 200.8

200.8 Dissolved Metals	10.13	Method 200.8
3050B Special Sb prep	10.14	Method 6020

(See also WI-DV-017)

10.11 Method 3020A - Preparation for Total Metals Analysis by ICP-MS Method 6020 and 6020A

10.11.1 To the sample in a digestion tube, add 1.5 mL of concentrated HNO_3.

10.11.2 Heat at 90 - 95 °C until the volume is reduced to approximately 5 mL. Record the start time and the Hot Block temperature in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared and reanalyzed.

10.11.3 Allow the digestion tube to cool in a fume hood.

10.11.4 Add 1.5 mL of concentrated HNO_3. Cover and reflux gently.

10.11.5 Continue heating, adding additional acid as necessary in 1-2 mL increments to ensure a complete digestion. Record the start and stop times and the Hot Block temperature in TALS.

NOTE: Digestion is complete when the digestate is light in color and does not change in appearance with continued refluxing.

10.11.6 Evaporate to low volume, approximately 3 - 5 mL.

10.11.7 Allow the digestion tube to cool, then add about 10 mL of reagent water.

10.11.8 Replace the cover and continue warming for 10 to 15 minutes to allow additional solubilization of any residue to occur. Record the stop time in TALS.

10.11.9 Allow the sample to cool and rinse the watch glass into the digestion tube with reagent water.

10.11.10 Re-Volume to 50 mL with reagent water, cap and mix thoroughly.

10.11.11 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0018 or DV-MT-0022.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis. Refer to SOP DV-MT-0018 or DV-MT-0022 for additional details.

10.12 Method 3005A - Preparation for Total Recoverable and Dissolved Metals Analysis by ICP-MS Method 6020 and 6020A

10.12.1 To the sample in a digestion tube, add 2.0 mL of concentrated HNO_3.

10.12.2 Heat the sample to 90 - 95 °C and cautiously evaporate to a low volume of 15 - 20 mL, while ensuring that no portion of the sample container is allowed to go dry. Record the start and stop times and the Hot Block temperature in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.12.3 Allow the sample to cool in a fume hood.

10.12.4 Rinse the digestion tube with reagent water.

10.12.5 Re-Volume to 50 mL with reagent water, cap and mix thoroughly.

10.12.6 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0018.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis. Refer to SOP DV-MT-0018 or DV-MT-0022 for additional details.

10.13 Method 200.8 - Preparation for Total Recoverable/Potentially Dissolved/Dissolved Metals Analysis by ICP-MS

10.13.1 To the sample, add 0.5 mL of concentrated HNO_3 and 0.25 mL of concentrated HCl.

10.13.2 Adjust the digestion block temperature so the solution in a covered container rises to approximately 90 - 95 ºC. Record temperature on bench sheet.

10.13.3 Heat the sample until it evaporates to approximately 10 mL, while ensuring that no portion of the bottom of the digestion tube is allowed to go dry.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.13.4 Cover the sample and gently reflux for an additional 30 minutes. Avoid vigorous boiling to prevent the loss of the HCl-H_2O azeotrope. Record the start and stop times and the Hot Block temperature in TALS.

10.13.5 Allow the sample to cool in a fume hood.

10.13.6 Rinse the watch glass or cover into the container and re-volume to 25 mL with reagent water. Cap and mix thoroughly.

NOTE: If the samples are being prepared to satisfy drinking water compliance requirements, bring the samples to a final volume of 50 mL before capping and mixing. Samples logged for this purpose will have attached TALS Method Comments to that effect.

10.13.7 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0002.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis. Refer to SOP DV-MT-0002 for additional details.

10.14 Method 3050B – Special Prep for Sb, Sn and Ag for Analysis by ICP-MS Method 6020

10.14.1 To 25 mL of sample in a digestion tube, add 2.5 mL of HNO_3 and 2.5 mL of HCl.

10.14.2 Heat at 90-95 °C until the sample has reduced to a volume of 10-15 mL ensuring that no portion of the sample container is allowed to go dry.

Record the start and stop times and the Hot Block temperature in TALS.

10.14.3 Remove the sample from the Hot Block and allow it to cool in a fume hood.

10.14.4 Add 1.0 mL of HCl to the digestion tube and cover with a ribbed watch glass.

10.14.5 Replace the watch glass and heat the sample for 15 minutes.

Record the start and stop times and the Hot Block temperature in TALS.

10.14.6 Remove the sample from the Hot Block and allow it to cool in a fume hood.

10.14.7 Re-volume to 100 mL with reagent water, cap and mix thoroughly.

10.15 Calibration

The digestion block temperature must be maintained between 90 and 95 °C. The temperature must be monitored continuously while in use and must be recorded on the metals preparation bench sheet. The temperature must be monitored by measuring the temperature of reagent water contained in a digestion tube that is placed in each digestion block. The thermometer used and the start and end time temperatures are recorded in TALS. The thermometer is calibrated in accordance

with SOP DV-QA-0001, *Thermometer Calibration Procedures*.

11.0 Calculations / Data Reduction

11.1 Not applicable. See the determinative method SOPs, DV-MT-0002, DV-MT-0018 and DV-MT-0022 for data analysis and applicable calculations.

11.2 Documentation

11.2.1 All of the preparation information is recorded and stored in TALS.

11.2.2 The preparation information includes:

11.2.2.1 Batch number, job and sample numbers, preparation date, and analyst name;

11.2.2.2 Matrix and prep type;

11.2.2.3 Initial sample pH, Initial sample volume and final volume;

11.2.2.4 Reagent manufacturer and lot number for each reagent used;

11.2.2.5 Digestion tube lot information;

11.2.2.6 Standard identification number for each standard used;

11.2.2.7 Start and stop times for digestions;

11.2.2.8 Observed and corrected temperature readings during digestion;

11.2.2.9 Identification numbers of calibrated measuring equipment used (thermometers, balances, pipettes, etc.).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

13.1 This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produce when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards: Contact Waste Coordinator

14.2.2 Acidic waste from sample digests: Waste Stream J.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.1.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.2 Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, Revision 1, July 1992.

15.1.3 Method 6020, Inductively Coupled Plasma - Mass Spectrometry, Revision 0, September 1994.

15.2 Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

15.3 Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectroscopy, Revision 5.4, May 1994.

16.0 Method Modifications:

16.1 Modifications and Interpretations Applicable to SW-846 Reference Methods

16.1.1 Chapter 1 of SW-846 states that the method blanks should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above one-half of the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

16.1.2 The referenced methods, as well as Table 3-1 of SW-846, refer to the use of a 100-mL aliquot for digestion. This SOP requires the use of a 50-mL sample size to reduce waste generation. The use of reduced sample volumes is supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition", dated November 3, 1994. This document stated, "...flexibility to alter digestion volumes is addressed and 'allowed' by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..."

EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a

significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Oliver Fordham stated. " As a 'representative sample' can be assured, scaling causes no loss of precision and accuracy in the analysis."

16.2 Modifications Specific to Method 3005A

An additional 1.0 mL of HNO_3 was included to replace the 5.0 mL of HCl. HCl was eliminated to reduce interferences from chloride.

16.3 Modifications and Interpretations Specific to Method 3020A

16.3.1 Section 10.11.6 of this SOP requires that the sample be reduced to a volume of 3-5 mL. Section 7.2 of Method 3020A states that the volume should be reduced to 3 mL, but also states that no portion of the bottom of the digestion tube should go dry. The volume required by this SOP is a closer approximation of the volume required to provide an adequate covering of the bottom of the digestion tube so as to prevent the loss of critical analytes through volatilization.

16.3.2 The scope of 3020A has been expanded to include silver, based on comparison studies with 7760A. Method 3020A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water, and TCLP leachate) up to a concentration of 1 ppm silver.

17.0 Attachments

Table 1. TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels
Table 2. Summary of Quality Control Requirements
Appendix A. Contamination Control Guidelines

18.0 Revision History

- Revision 10, Dated 31 October 2017
  - Annual Review
  - Removed Note about sample count for AFCEE

- Revision 9, Dated 30 September 2016
  - Annual Review
  - Removed reference to Method 3050 from title page and Sections 1.1 and 15.
  - Removed Acceptance Criteria and Corrective Actions for QC samples from Section 9. These are addressed in each determinative SOP.
  - Updated Section 10.9.1.4 preservation time to 24 hours
  - Added method blank to section for filtration if samples are filtered. All QC must be treated the same.
  - Revised Section 12 to reflect current practice
  - Revised Table 2 to include all determinative method SOPs

- Revision 8, Dated 30 September 2015
  - Added drinking water to Section 1.6.
  - Corrected Section reference tables.
  - Added note to Section 10.13.6 describing changed final volume requirement.

- Revision 7, Dated 30 June 2015
  - Updated Section 10.13.2 for temperature requirement of 90-95 for method 200.8
  - Updated Section 10.9.1.1 for proper technique when using pH paper.
  - Added new Section 10.8 reminding analysts to enter data directly at time of acquisition
  - Added Section 11.2 describing required data to be recorded
  - Removed Section 11.4

- Revision 6, Dated 29 September 2014
  - Annual review
  - Removed references to microwave procedure
  - Removed direct-shoot for dissolved analysis
  - Corrected section references
  - Replaced LIMS and Standards Log references with TALS
  - Clarified the number of MS/MSDs per prep batch based on method
  - Removed workflow diagrams Figures 1-4
  - Removed Tables 1 and 2
  - Minor spelling and language corrections throughout

- Revision 5, Dated 30 September 2013
  - Reference to SOP DV-IP-0017 for preparation of organic waste
  - Formatting updates
  - Updated section 9, 12 & 14 to include more detail
  - Annual review
  - Updated sections 10.8.1.2 - 10.8.1.4 to removed reference to amount of HNO_3 acid added.
  - Added to Section 10.8.1.6 that a maximum of 5mls of HNO_3 can be added.

- Revision 4, Dated 28 September 2012
  - Annual review
  - Section 9.6 Updated method blank control limits to ½ the reporting limit.
  - Updated appendix B with revised Work Instruction.

- Revision 3.5, dated 23 September 2011
  - Annual Technical Review
  - Removed reference to Supplemental Metals Prep Sheets in Sections 10.10.8 and 10.13.5.1
  - Removed reference to Clouseau in Section 10.8.1.2
  - Removed references to LIMS codes in Appendix B

Earlier revision histories have been archived and are available upon request.

Table 1.

TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

Table 2.

Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per sample preparation batch of up to 20 samples	Refer to Determinative SOP: 200.8: DV-MT-0002 6020: DV-MT-0018 6020A/B: DV-MT-0022	Re-digest and reanalyze samples associated with the method blank
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples	Refer to Determinative SOP: 200.8: DV-MT-0002 6020: DV-MT-0018 6020A/B: DV-MT-0022	Re-digest and reanalyze samples associated with the method blank
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples	Refer to Determinative SOP: 200.8: DV-MT-0002 6020: DV-MT-0018 6020A/B: DV-MT-0022	Re-prep not required unless preparation error suspected.
Matrix Spike Duplicate (MSD)	See Matrix Spike frequency	Refer to Determinative SOP: 200.8: DV-MT-0002 6020: DV-MT-0018 6020A/B: DV-MT-0022	See Corrective Action for Matrix Spike

Appendix A.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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